doi:10.1017/S1431927617005323
Microsc. Microanal. 23 (Suppl 1), 2017
© Microscopy Society of America 2017

In situ Analytical Microscopy of Asphaltene Aggregation and Growth

Nestor J. Zaluzec[1,2,] Arne Janssen[2], Matthew A. Kulzick[3], and M.G. Burke[2]

[1]Photon Sciences Division, Argonne National Laboratory, Il, USA
[2]Materials Performance Centre, School of Materials, The University of Manchester, Manchester, UK.
[3]BP Corporate Research Centre, Naperville Il, USA

Asphaltenes are precipitated solids found in crude oils that are composed of aromatic hydrocarbons and small amounts of non-volatile species (S,K, Ca, P, V, Ni, Zn, ….) which when they form accumulate as deleterious deposits in piping used to transport and/or store oil. Their presence adversely affects viscosity, and interfacial properties of oils and their evolution from individual molecular species into aggregates and finally into very large deposits is a challenge to fully characterize. Their formation is a dynamic process involving both morphological and chemical changes as a function of temperature, pressure and initial crude oil composition. The molecular and colloidal structure of asphaltenes have been the subject of numerous studies, and various models have been proposed [1]. The Yen-Mullins model, proposes that there are three stages: firstly small ~ 1 nm molecular particles; followed by nanoaggregates and finally massive clusters which range from hundreds of nanometers to macroscopic dimensions [2,3].

TEM studies of asphaltenes have been conducted to understand the mechanisms of flocculation, aggregation and precipitation [4,5]. *In situ* studies of emulsions using analytical TEM permits direct studies of the asphaltenes at the nm scale while still emersed in oil emulsions, with minimal sample pre-treatments and is a the subject of this continuing experimental study. The TEM experiments reported herein were conducted in a FEI Talos F200X Analytical TEM equipped with a SuperX SDD X-ray detector system at Manchester University and a Protochips Poseidon P210 analytical liquid cell holder [5]. Middale Canadian crude oil was mixed with heptane at a 40:1 ratio to initiate precipitation of the asphaltenes in the liquid *in situ* cell. This mixing is a standard protocol in the industry to accelerate the flocculation process. Figure 1 shows the an early stage of formation of asphaltene nanoaggrates in an oil + heptane emulsion in the liquid cell, encapsulated between two 50 nm thick SiNx windows. The initial stages of asphaltene formation was not observable due to the delay (~ 1 hr) in getting the oil/heptaine mixture into the Poseiden holder, sealed and then into the microscope. In figure 1, the formation of long stringers of coalesced nanoaggregates which were C,O and S rich was readily apparent. To study the later stages of formation, the same oil was allowed to remain in the Heptane oil mixture for 7 days, after which it was vacuum filtered through 200 micron sieves to isolate the asphaltenes which had increased in size and number. These larger deposits which were too large for encapsulation in our small gap SiNx eCell, were fortunately stable in both air and vacuum and were drop cast on to SiNx films, allowed to settle for 12 hours. After which they were rinsed in Heptane to remove any residual oil coating, and the Heptane allowed to dry in air for 2 hours, before examination in the Analytical TEM. Figure 2 illustrates the two structure which forms, one of which is a dense consolidated mass rich in Sulphur, and the other a interconnected network of higher Carbon content stringers. Both of which are stable under the even the most intense electron beam irradiation. Intermediate experiments to identify the transition/nucleation point of the phase separation are underway.

References:

[1] Hesseini-Dastgerdi *et al*, Asia Pacific Journal of Chemical Engineering, **10**, (2014), p. 1-14.

https://doi.org/10.1017/S1431927617005323 Published online by Cambridge University Press

[2] Dickie & Yen, Analytical Chemistry, **39**, (1967), 1847-1852.
[3] Mullins, Energy & Fuels, **24**, (2010), p. 2179-2207
[4] L. Goual *et al*, Langmuir, **30**, (2014), p. 5394-5403.
[5] Janssen etal, Microsc. Microanal. 22 (Suppl 3), (2016) 796-797 doi:10.1017/S1431927616004839
[6] We acknowledge BP for financial funding at University of Manchester. Part of this work was supported by Office of Science, Contract No. DE-AC02-06CH11357 in the Photon Sciences Division at Argonne National Laboratory

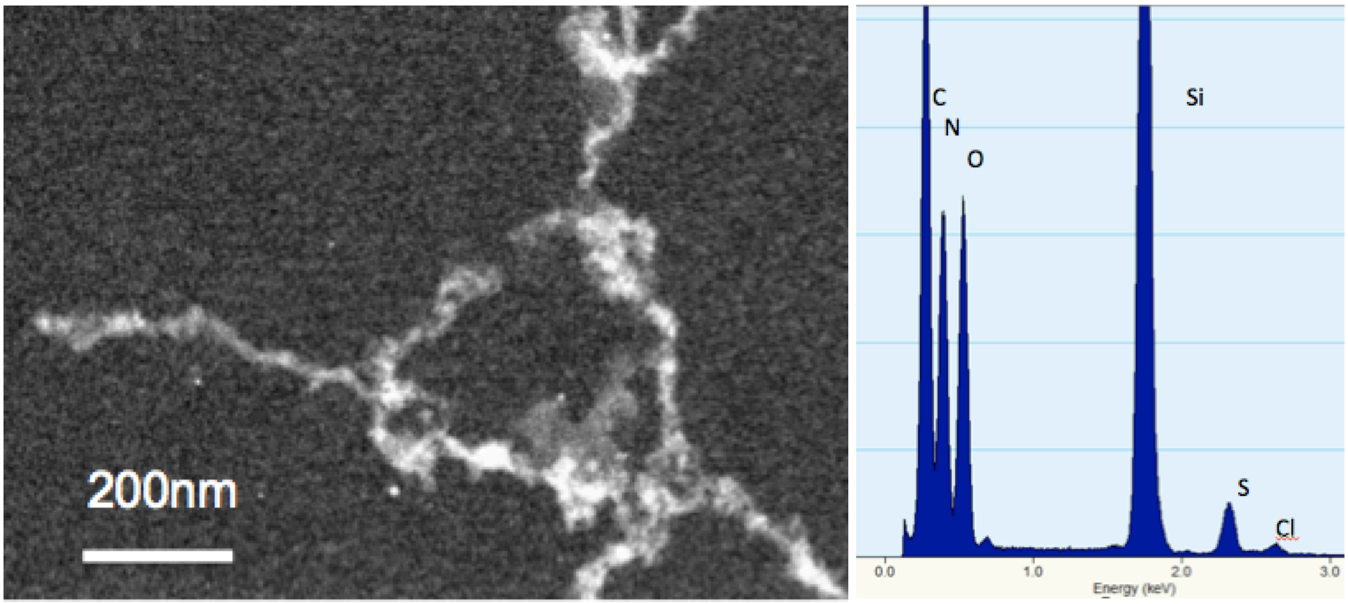

Figure 1. *In situ* STEM-HAADF images showing the agglomeration of ~ 20 nm diameter asphaltene stringers into extended structures. In-situ XEDS, demonstrates these are aggregates principly C,O, and S; the Si, N, and Cl signals arise from the liquid cell window.

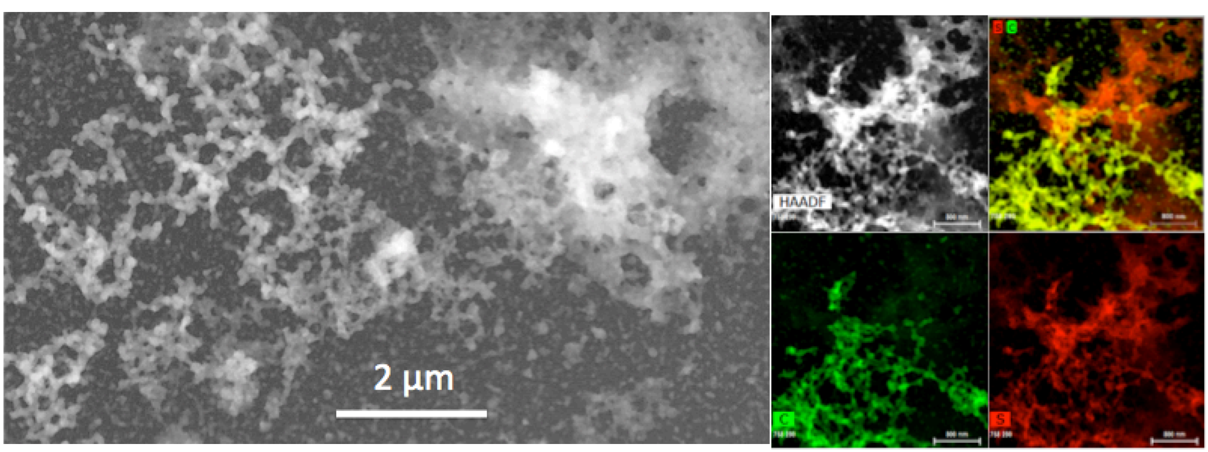

Figure 2. HAADF STEM image of densified two phase structure and C,S XEDS map. The solid mass is higher in Sulphur, while the interconnected network higher in Carbon. Both phases contain C, S, O as well as trace amounts of various transition metals.

https://doi.org/10.1017/S1431927617005323 Published online by Cambridge University Press